cm^{-1}; λ_{max} (CH_3OH) 206 mμ (ϵ 118) and 245 (186); nmr (CCl_4) δ 1.33 (t, 3, CH_3), 4.33 (q, 2, CH_2), and 6.95 ppm (broad s, 1, NH).

Sodium Salt of MCU.—To a methanol solution of sodium hydroxide (0.8 g, 0.02 mol), MCU (2.5 g, 0.02 mol) was added dropwise with stirring at 0°. When addition was complete, the reaction mixture was evaporated to dryness in a rotary vacuum evaporator at room temperature. The crude residue was washed with ether, and the residue was again evaporated to yield the anhydrous sodium salt, a hygroscopic white solid (2.7 g, 98.7% yield). Purity by iodometric analysis exceeded 99%. The salt did not decompose on heating to 250°: ir (KBr pellet) 1600 (C═O), 1360, 1260 (ester), 1080 (ester) and 770 (C—Cl) cm^{-1}; λ_{max} (CH_3OH) 205 mμ (ϵ 267); nmr (DMSO-d_6) δ 1.07 (t, 3, CH_3) and 3.83 ppm (q, 2 H, CH_2).

Potassium Salt of MCU.—Prepared from equimolar quantities of MCU and potassium hydroxide, as just described for the sodium salt, except that it was purified by pouring the half evaporated methanol solution into ether. The anhydrous potassium salt, a hygroscopic white solid, was obtained as a precipitate (yield 96%; purity >96%). It did not decompose on heating to 250°: ir (KBr pellets) 1600 (C═O), 1360, 1270 (ester), 1075 (ester) and 770 cm^{-1} (C—Cl); λ_{max} (CH_3OH) 211 mμ (ϵ 1030); nmr (DMSO-d_6) δ 1.05 (t, 3, CH_3) and 3.78 ppm (q, 2, CH_2).

Silver Salt of MCU.—A 1% aqueous solution of silver nitrate (1.2 g, 0.007 mol) was added dropwise to a 1% aqueous solution of the sodium salt of MCU (1.0 g, 0.007 mol) with stirring at room temperature in the dark. The precipitate was filtered, washed with methanol and dried under vacuum in the dark. A white crystalline solid unstable to light was obtained (yield 100%; purity >99.0%). The anhydrous silver salt decomposed violently on heating to 127°: ir (KBr pellets) 1600 (C═O), 1360, 1270 (ester), 1075 (ester) and 768 (C—Cl) cm^{-1}.

Lithium Salt of MCU.—Attempts to prepare the lithium salt were unsuccessful. Reaction of MCU at 0° with lithium hydroxide in methanol yielded an unstable colorless liquid that decomposed at room temperature with evolution of a gas over a period of several days. The freshly prepared oil gave a precipitate on treatment with aqueous silver nitrate suggesting that some lithium salt may have formed (MCU does not react with silver nitrate). Similar results were obtained on reaction of MCU with *n*-butyllithium at −76° in tetrahydrofuran with cyclohexene present.

Reaction of Metallic Salts of MCU with Cyclohexene.—A mixture of the sodium salt of MCU (10 g, 0.069 mol) and cyclohexene (282 g, 3.45 mol) was placed in a 500-ml flask equipped with a stirrer, thermometer, condenser, and gas inlet tube. The mixture was then refluxed under nitrogen for 48 hr. The insoluble matter was filtered, washed with ether, and dried under vacuum. It was shown by analysis to be a mixture of sodium chloride and the unreacted sodium salt of MCU. (By iodometric analysis, only 60% of the sodium salt of MCU had decomposed.) After removing ether and unreacted cyclohexene from the filtrate, the liquid residue was cooled to 0° to precipitate a very small yield of colorless needles. They were recrystallized from *n*-hexane and shown to be 1,1,1-trichloroethylbis(carbamate) (I): mp 172–172.5°; ir (KBr) 3260 (NH), 2990 (CH), 1700 (C═O) and 825 cm^{-1}; nmr ($CDCl_3$) δ 1.28 (t, 6, CH_3), 4.22 (q, 4, CH_2), 5.56 (broad, d, 2, NH), and 6.61 ppm (d, 1, CH).

Anal. Calcd for I: C, 31.24; H, 4.26; Cl, 34.58; N, 9.11; O, 20.81. Found: C, 31.42; H, 4.07; Cl, 34.85; N, 9.41; O, 20.15.

The hexane filtrate was washed with water to remove ethylurethan and then distilled under vacuum. A main fraction, azabicyclo[4.1.0]heptane, was obtained in very low yield at 31.0–32° (0.4 mm): ir (neat) 3350 (NH), 2920, 2850, 1440, 1020 and 882 cm^{-1}; nmr (CCl_4) δ 1.37 (m, ring CH_2), 1.79 (m, ring CH_2), 3.65 (broad s, ring CH), and 4.28 ppm (broad s, NH); singlet at 4.28 ppm disappears when the solution is treated with D_2O solution containing a trace of trifluoroacetic acid. The ir and nmr were identical with those of an authentic sample.

Reaction of the Sodium Salt of MCU with Acetone.—A mixture of the sodium salt (13 g, 0.089 mol) and acetone (254 g, 4.45 mol) was refluxed for 18 hr; 96% of the sodium salt decomposed. After sodium chloride was separated by filtration, the liquid product was distilled under reduced pressure; after removal of acetone a fraction was obtained as a colorless liquid (12 g) at 65.5–66.5° (13 mm), identified as diacetone alcohol by ir and nmr. The residue was dissolved in hot *n*-hexane and cooled to yield ethylurethan (4.9 g, 62% yield).

Registry No.—MCU, 16844-21-6; sodium salt of MCU, 17510-52-0; potassium salt of MCU, 17510-53-1; silver salt of MCU, 17510-54-2; I, 17528-34-6.

The Addition of Dimethylketene to Trichloroacetyl Chloride. A β-Keto Acid Halide[1]

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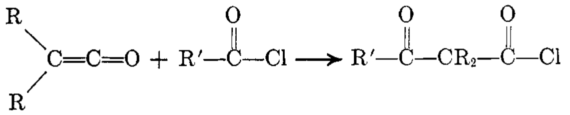
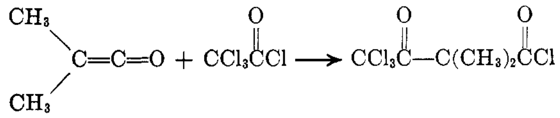
Staudinger and coworkers were the first to describe the addition of an acid chloride to a ketene to produce a β-keto acid halide[2] (eq 1). While this reaction has


$$\mathrm{R_2C{=}C{=}O} + \mathrm{R'{-}\overset{O}{\overset{\|}{C}}{-}Cl} \longrightarrow \mathrm{R'{-}\overset{O}{\overset{\|}{C}}{-}CR_2{-}\overset{O}{\overset{\|}{C}}{-}Cl} \qquad (1)$$

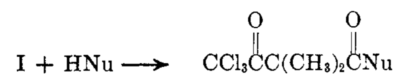
been investigated, in most cases the β-keto acid halide was not isolated but converted into an ester.[3,4] Therefore, we wish to report the results of an investigation on the addition of dimethylketene to trichloroacetyl chloride and the isolation, characterization, properties, and chemical reactivity of the resultant β-keto acid halide.

Dimethylketene readily reacts with trichloroacetyl chloride at room temperature to produce 4,4,4-trichloro-2,2-dimethyl-3-ketobutanoyl chloride (I) in 61% yield (eq 2). The structure of I was proven by a combination of elemental analysis and infrared (ir) and proton magnetic resonance (pmr) spectra. An ir band at 1785 revealed that the adduct was an acid halide and a band at 1740 cm^{-1} verified the presence of the β-keto group. The pmr spectrum revealed the methyl protons at 1.77 ppm.


$$\mathrm{(CH_3)_2C{=}C{=}O} + \mathrm{CCl_3\overset{O}{\overset{\|}{C}}Cl} \longrightarrow \mathrm{CCl_3\overset{O}{\overset{\|}{C}}{-}C(CH_3)_2\overset{O}{\overset{\|}{C}}Cl} \qquad (2)$$

I

Compound I readily undergoes the expected nucleophilic substitutions as illustrated in eq 3.


$$\mathrm{I + HNu} \longrightarrow \mathrm{CCl_3\overset{O}{\overset{\|}{C}}C(CH_3)_2\overset{O}{\overset{\|}{C}}Nu} \qquad (3)$$

II, Nu = OCH_3
III, Nu = OH
IV, Nu = $NHCH_2C_6H_5$
V, Nu = NHC_6H_5

It is interesting to note that I reacts with an equimolar amount of benzylamine to produce the expected N-benzylamide (IV), but, when treated with an excess of amine, N,N′-dibenzyldimethylmalonamide (VI) is

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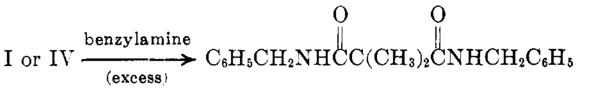
[1] This work was supported by a National Science Foundation Grant GP-7386.

[2] H. Staudinger, O. Gohring, and M. Scholler, *Ber.*, **47**, 40 (1914).

[3] F. Sorm, J. Smrt, and J. Beranek, *Chem. Listy.*, **48**, 679 (1954).

[4] F. Sorm, J. Smrt, and J. Beranek, *ibid.*, **49**, 73 (1955).

produced. Also, treatment of IV with benzylamine will produce VI (eq 4). Apparently, this reaction is



$$\text{I or IV} \xrightarrow[\text{(excess)}]{\text{benzylamine}} C_6H_5CH_2NH\overset{O}{\overset{\|}{C}}C(CH_3)_2\overset{O}{\overset{\|}{C}}NHCH_2C_6H_5 \quad (4)$$

VI

analogous to the familiar iodoform reaction of methyl ketones.

Experimental Section

Dimethylketene was prepared by the pyrolysis of the commercially available ketene dimer, tetramethyl-1,3-cyclobutanedione, and then distilled just prior to the addition reaction.[5] All of the solvents used in this study were dried by refluxing and distilling from lithium aluminum hydride through a 30-plate Oldershaw column. The pmr spectra were recorded on a Varian A-60 instrument.

4,4,4-Trichloro-2,2-dimethyl-3-ketobutanoyl Chloride. (I).—A solution of 2.6 g of dimethylketene (0.037 mol) in 25 ml of hexane was added slowly to a stirred solution of 10 ml (0.0912 mol) of trichloroacetyl chloride in 50 ml of hexane at room temperature. After standing overnight, the solvent was removed under reduced pressure, and the residue was fractionated to yield 5.7 g (61%) of I at 68–70° (0.7 mm). The spectral data were given above.

Anal. Calcd for $C_6H_6Cl_4O_2$: C, 28.55; H, 2.20. Found: C, 28.55; H, 2.10.

Methyl 4,4,4-Trichloro-2,2-dimethyl-3-ketobutanoate. (II).—A 2-g (0.0079 mol) portion of I was added dropwise with stirring to an excess of dry methanol at room temperature. The excess methanol was evaporated, and the residue was recrystallized from ligroin to yield 1.7 g (91%) of II: mp 42–43°; ir 1755 and 1740 cm^{-1}; pmr (CCl_4) a singlet at 3.75 and 1.60 ppm. The peak areas were in the ratio of 1:2.

Anal. Calcd for $C_7H_9Cl_3O_3$: C, 33.90; H, 3.63. Found: C, 33.75; H, 3.72.

4,4,4-Trichloro-2,2-dimethyl-3-ketobutanoic Acid (III).—The dropwise addition of I to an excess of water resulted in a quantitative conversion into III which was recrystallized from ligroin: mp 115–116°; ir 1710 cm^{-1}.

Anal. Calcd for $C_6H_7Cl_3O_3$: C, 30.86; H, 3.02. Found: C, 30.95; H, 2.72.

N-Benzyl-4,4,4-trichloro-2,2-dimethyl-3-ketobutanamide (IV).—A solution of 0.75 g (0.00297 mol) of I in 25 ml of dry hexane was added dropwise to a stirred solution of 0.318 g (0.00297 mol) of benzylamine in 10 ml of dry hexane. A white precipitate formed upon addition. The reaction mixture was washed with dilute hydrochloric acid solution, followed by a water wash. Drying and evaporation of the solvent yielded 0.4 g of IV. This material was recrystallized from 70% ethanol: mp 100.5–102°; ir 1745 and 1635 cm^{-1}.

Anal. Calcd for $C_{13}H_{14}Cl_3NO_2$: C, 48.40; H, 4.34. Found: C, 48.45; H, 4.51.

N-Phenyl-4,4,4-trichloro-2,2-dimethyl-3-ketobutanamide (V).—The anilide was prepared in the same manner as described above for the N-benzamide, except ether was used as the solvent. Recrystallization from ligroin yielded crystals with mp 146–147°; ir 1745 and 1635 cm^{-1}.

Anal. Calcd for $C_{12}H_{12}Cl_3NO_2$: C, 46.6; H, 3.89. Found: C, 46.86; H, 3.61.

N,N′-Dibenzyldimethylmalonamide (VI).—A 3.5-g (0.0139 mol) portion of I was added dropwise with stirring to a solution of 5 g (0.0467 mol) of benzylamine in 250 ml of benzene. The reaction mixture was washed with dilute hydrochloric acid solution, followed by water. The benzene solution was dried over anhydrous magnesium sulfate, filtered, and cooled to yield 3.5 g (81%) of VI. The crude product was recrystallized from 70% ethanol to yield small white needles, mp 166–167°. A mixture melting point with an authentic sample of VI prepared from dimethylmalonyl chloride and benzylamine showed no depression.

Anal. Calcd for $C_{19}H_{22}N_2O_2$: C, 73.50; H, 7.10; mol wt, 310. Found: C, 73.50; H, 7.18; mol wt, 310 (mass spectrum).

Compound VI could also be prepared by treatment of IV with an excess of benzylamine.

Registry No.—I, 17953-83-2; II, 17953-84-3; III, 17953-85-4; IV, 17953-86-5; V, 17953-87-6; VI, 17953-88-7; Me_2CCO, 598-26-5; Cl_3CCOCl, 76-02-8.

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Reactions of Phenyl Isocyanate and Phenyl Isothiocyanate with Indole and Metal Derivatives of Indole

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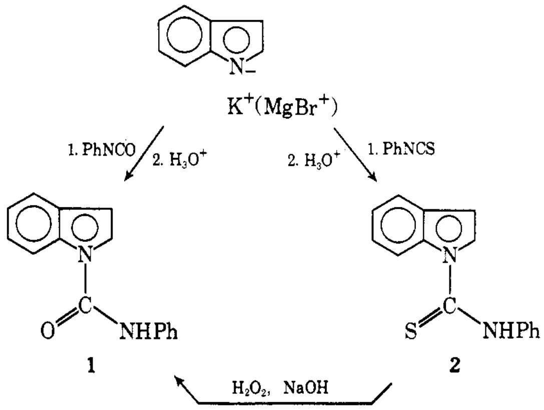
Pyrrole is known to react with phenyl isocyanate and phenyl isothiocyanate to form 2-pyrrolecarboxanilide[1] and 2-pyrrolethiocarbanilide,[2] respectively. With the same reagents, pyrrolylpotassium forms the 1-carboxanilide and 1-thiocarbanilide, whereas pyrrolylmagnesium bromide gives mixtures of the 1 and 2 derivatives.[3,4]

We wish to report now on the analogous reactions of indole, indolylpotassium, and indolylmagnesium bromide. When treated with phenyl isocyanate or phenyl isothiocyanate in tetrahydrofuran, indolylpotassium yields 1-indolecarboxanilide (1) or 1-indolethiocarbanilide (2). It is noteworthy that the same compounds are obtained from the corresponding reactions of indolylmagnesium bromide in tetrahydrofuran, despite the general tendency of this reagent to give 3-substituted indole derivatives.[5] Comparison of the infrared spectra of the crude and purified products shows that these reactions lead to the formation of 1-substituted indole derivatives only. The structure assigned to 1 is consistent with its infrared spectrum, which shows a carbonyl absorption at 1710 cm^{-1}, but not the characteristic indole N–H band in the 3400–3500-cm^{-1} region.[6] Furthermore, alkaline hydrolysis of 1 yields a mixture of indole and aniline. The structure of 2 is confirmed by its smooth oxidation to 1 with alkaline hydrogen peroxide.



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[3] E. P. Papadopoulos and H. S. Habiby, *J. Org. Chem.*, **31**, 327 (1966).

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[5] M. H. Palmer, "The Structure and Reactions of Heterocyclic Compounds," Edward Arnold Ltd., London, England, 1967, p 324.

[6] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed, John Wiley & Sons, Inc., New York, N. Y., 1962.